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Final Technical Report

Grant Number:
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Title:
Measurement of helical trajectories in chemical reactions by ion imaging.

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DOE Patent Clearance Granted
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14 May 2003

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Requested Budget:
$149,942 (three years)

Progress:

During the first year of this grant we developed methods to measure the sense of rotation of the nitric oxide molecule (NO) using a circularly polarized laser probe and with ion imaging detection. The method was applied to the measurement of the correlation of rotational angular momentum orientation with recoil direction in the photodissociation of NO_2. ["Detection of 'ended' NO recoil in the 355 nm NO_2 photodissociation mechanism", V.K. Nestorov and J.I. Cline, *J. Chem. Phys.* 111, 5287-5290 (1999)]. The photodissociation work was performed at the University of Nevada with additional, partial support from NSF.

In the summer of 1999 this technique was transported to and implemented at the Combustion Research Facility at Sandia National Laboratory in Livermore, CA in a study of rotationally inelastic collisions of NO molecules with Ar atoms. The summer 1999 experiments at Sandia demonstrated that it is possible to detect collision-induced rotational alignment (preferred planes of rotation) for product molecules. During the late summer and fall of 1999 the P.I. and student James Barr developed a theoretical method for quantifying the angular momentum alignment and for extracting it from ion images.

During the winter and spring of 2000 (January-May) the P.I. was in residence at Sandia National Laboratory in Livermore during a sabbatical leave from the University of Nevada. During this time the P.I. collaborated with Sandia P.I. Dr. David Chandler and Sandia postdoctorals Thomas Lorenz and Elisabeth Wade in experiments measuring both rotational alignment and rotational orientation (preferred senses of rotation) in collisions of NO with Ar. Graduate student James Barr continued these experiments at Sandia through the end of June 2000. The success of our experimental techniques

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for measuring collisional alignment and the theoretical methods we have developed for extracting quantitative alignment parameters from ion images. One publication has come out on this alignment work ["Ion imaging measurement of collision-induced rotational alignment in Ar-NO scattering", J.I. Cline, K.T. Lorenz, E.A. Wade, J.W. Barr, and D.W. Chandler, *J. Chem. Phys.* **115**, 6277-6280 (2001)] and a second is in preparation at this time.

Spectroscopic probing of products by resonance-enhanced multiphoton ionization (REMPI) detected by ion imaging is a powerful method for measuring the product state-resolved differential cross section (DCS) of bimolecular scattering reactions. Polarization of the REMPI probe light also makes imaging data potentially sensitive to product angular momentum polarization, as is well known from imaging studies of photodissociation. We exploit this sensitivity to obtain the state-resolved product angular momentum polarization as a function of recoil angle. Previous measurements of molecular angular momentum polarization in bimolecular scattering have either been constrained to detection in the scattering plane or have averaged around the azimuthal angle of the recoil velocity vector in the collision frame. Imaging detection captures the entire product recoil velocity sphere, enabling a more complete determination of product angular momentum polarization than is possible for experiments of lower detection dimensionality.

In our first experiments we studied rotationally inelastic collisions between ground state NO and Ar atoms,

$$\mathrm{NO}\ ^2\Pi_{1/2}(v=0, j=1/2) + \mathrm{Ar} \rightarrow \mathrm{NO}\ ^2\Pi_{1/2}(v'=0, j'>1/2) + \mathrm{Ar}, \qquad E_{col} = 65\ \mathrm{meV}.$$

The experiments were conducted in a crossed molecular beam apparatus at Sandia with two-color, polarized $1+1'$ REMPI probing of rotational alignment of NO on its $A \leftarrow X$ transition. Rotationally state-selected NO^+ cations were velocity-map imaged onto a two-dimensional position sensitive detector. In alignment measurements, imaging data was collected at two polarization geometries in which the the probe pulse electric vector, ϵ_p, was either parallel (V) or perpendicular (H) to the detection axis.

As an example, Fig. 1 below shows velocity-mapped NO^+ images measured for the $R_{21}(8.5)$ line of the probe transition. Image (a) was obtained in the V polarization geometry, and the gray scale shading increases with NO^+ signal. The Newton diagram for the collision is superimposed. To facilitate quantitative intensity comparisons, histogrammed images are shown in (b) and (c) for the V and H polarization geometries, respectively (with contours at 5%, 10%, 15%, 20%, 30%, and 80% of full scale). Image (d) shows the measured $(V-H)/(V+H)$ scaled differences, where the shading increases with a positive difference ($V > H$). In images (d-f) the background shade corresponds to zero difference, $V = H$, and lighter shades to $V < H$. Measured and fit histogrammed $(V-H)/(V+H)$ images are shown in (e) and (f), respectively, with contours spaced by 0.05 over a ± 0.15 range.

In Fig. 1, the V image is more intense than H for strongly forward scattered NO, and less intense for the backscattered NO. The differences between the V and H images and DCS's arise from angular correlations among the NO initial velocity, $\mathbf{v}_{NO}$, its final recoil velocity $\mathbf{v}'_{NO}$, and its final angular momentum, $\mathbf{j}'$. To focus on probe polarization differences, we construct a scaled difference image by computing the quantity $(I_V - I_H)/(I_V + I_H)$ from the intensities I_V and I_H at corresponding pixel locations in the V and H images. The $(V-H)/(V+H)$ image is insensitive to the DCS and to detectivity variations and therefore isolates the effect of angular momentum polarization. We use a semiclassical description to parameterize the angular correlation of $\mathbf{j}'$ in a center-of-mass helicity (HEL) frame, $x'y'z'$, defined so that $\hat{\mathbf{z}}' \| \mathbf{v}'_{NO}$ and the initial velocity $\mathbf{v}_{NO}$ lies in the $+x$ half of the $x'z'$ scattering plane defined by $\mathbf{v}'_{NO}$ and $\mathbf{v}_{NO}$. The probability distribution of $\mathbf{j}'$ in a frame attached to the scattering plane does *not* have cylindrical symmetry about the initial velocity, $\mathbf{v}_{NO}$.

At each Θ, we expand the angular distribution of $\mathbf{j}'$ in a basis of real spherical harmonics and the coefficients of the expansion are proportional to the real multipole moments $A_{Qp}^{(K)}$. These moments are "differential" quantities since they depend on the deflection angle, Θ. These quantities are obtained by a fit to the experimental data as seen in panels (e,f) of Fig. 1. The parameters extracted from these plots indicate that a "frisbee"-type $\mathbf{v}'_{NO} \perp \mathbf{j}'$ recoil trajectory is an important component of the dynamics at all deflection angles.

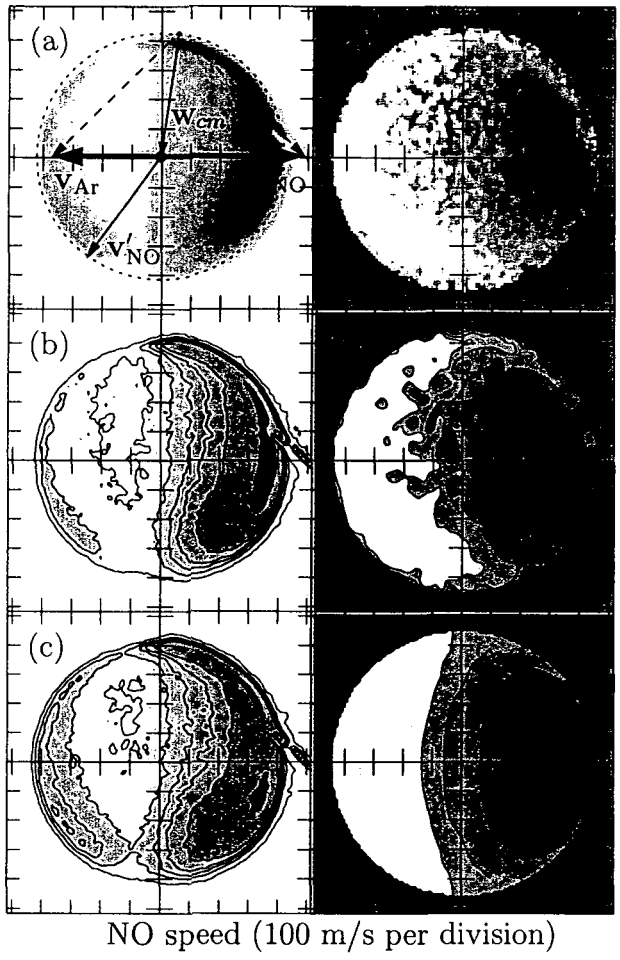

Figure 1: Imaging measurements of NO rotational alignment induced by collisions with Ar atoms.

Our next experiments used circularly polarized probe light to show that there is also a preferred sense (either clockwise or counter-clockwise) of rotation of the NO scattered to the left (or right) side of the relative velocity vector of the collision in the scattering plane. This was also a completely new type of experimental measurement and was published in the the prestigious journal *Science* ["Direct measurement of the preferred sense of NO rotation after collision with argon", K.T. Lorenz, D.W. Chandler, J.W. Barr, W. Chen, G.L. Barnes, and J.I. Cline, *Science* **293**, 2063-2066 (2001)]. The work also received widespread recognition in the general scientific press [for published commentary on this work, see: "Close encounters", F.F. Crim, *Science* **293**, 2014-2015 (2001); "News of the Week: Which way do they spin?", E. Wilson, *Chemical and Engineering News* **79**(38), 9 (17 Sep 2001); "Search and Discovery: Experiment and Theory Combine to Probe the Quantum Chemistry of Molecular Beams", C. Day, *Physics Today* **55**(1), 13-15 (Jan 2002)].

Figure 2 shows ion images similar to those in the first figure for the Ar-NO scattering system. In this case the difference images shown are obtained by subtracting an image taken with LCP (left circularly polarized) light from one obtained with RCP (right circularly polarized) light. There are alternations in the sign of the difference intensity in the $R - L$ images, which correspond to alternations in the preferred sense of rotation as a function of scattering angle, Θ. As described in the *Science* paper, this data was successfully modeled by *ab initio* quantum calculations and compared to classical trajectory simulations. The quantity $Q(\Theta)$ is a measure of the magnitude of the rotational orientation and can be obtained from the experimental images and computed theoretically. This quantity is shown in Fig. 2.

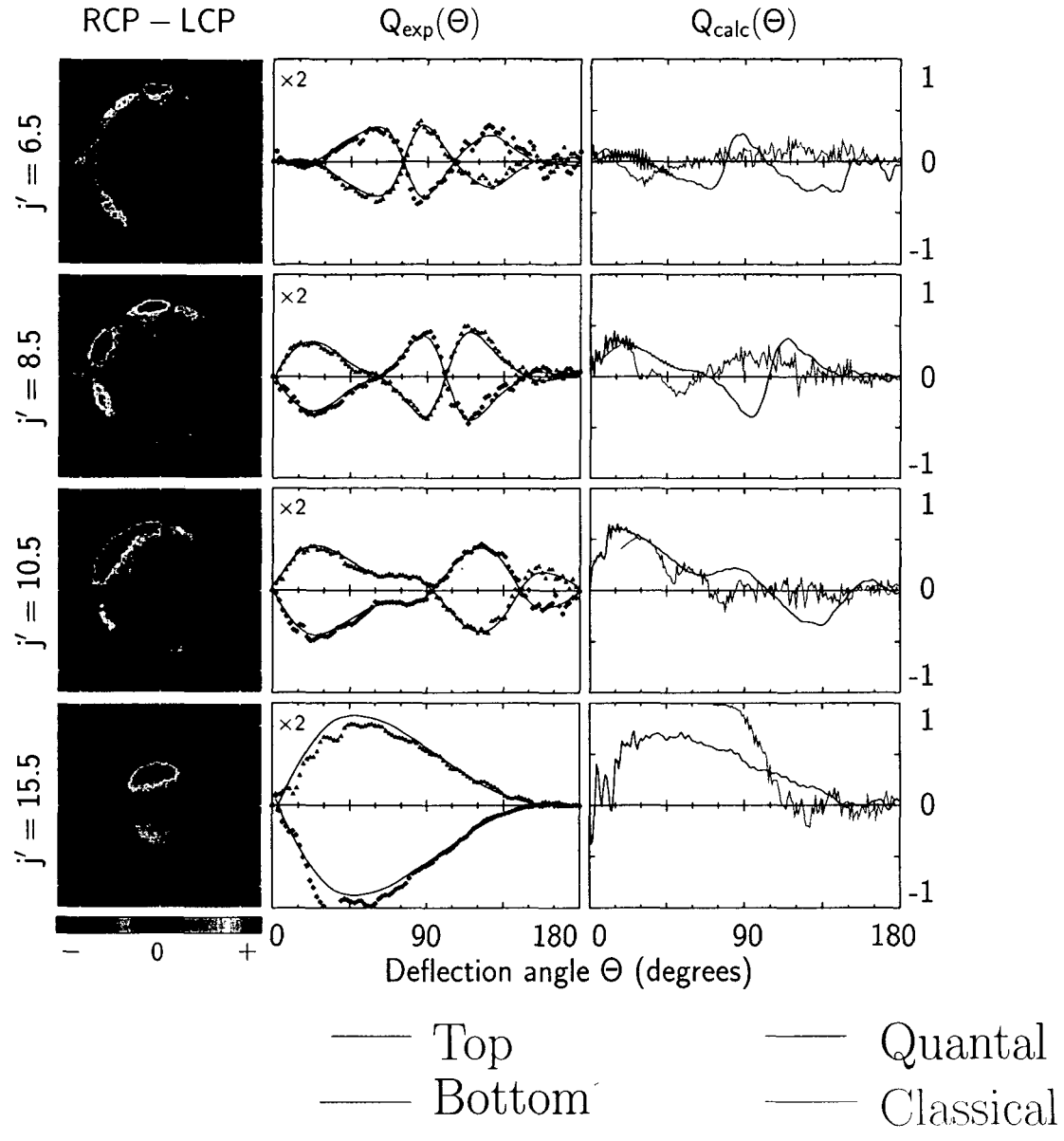

Figure 2: Imaging measurements of NO rotational orientation induced by collisions with Ar atoms.

The modeling work showed that quantum interference is a major contribution to the magnitude of the measured rotational orientation.

As part of this project we also made the first experimental direct measurement of the dissociation energy for the NO dimer (696 ± 4 cm^{-1}. This is an interesting quantity because NO is an open-shell species that might be expected to be distinct from ordinary van-der-Waals dimers or hydrogen-bonded dimers. The results of this experiment were published ["Direct measurement of the binding energy of the NO dimer", E.A. Wade, J.I. Cline, K.T. Lorenz, C. Hayden, and D.W. Chandler, *J. Chem. Phys.*, **116**, 4755-4757 (2002)].

Finally, the work performed under this project is the topic of a review publication that is currently in press: ["Ion imaging applied to the study of chemical dynamics", D.W. Chandler and J.I. Cline, in *Modern Trends in Chemical Reaction Dynamics – Part I*, ed. K.P. Liu and X.M. Yang (World

Scientific Pub.)]

Other work to be published:

As part of this project we also made scattering measurements on NO collisions with Ne and N_2. This data is currently being analyzed and will be published in the future along with our theoretical modeling of the results.

Future work in this collaboration could extend the study of rotationally inelastic collisions to reactive collisions such as $N + O_2 \rightarrow NO + O$.

Significant achievements:

1. We have made the first-ever imaging of the azimuthally-resolved rotational angular momentum alignment moments for a product molecule from bimolecular scattering. The measurements were made on the NO-Ar collision system. The results are qualitatively consistent with the conservation of rotational angular momentum along the kinematic apse vector of the collision.
2. We have made the first-ever measurements of rotational orientation of molecules in bimolecular collisions. The measurements were made on the NO-Ar collision system. For large rotational inelasticity, the dynamics are qualitatively similar to collisions of a particle with a hard-ellipsoid. At lower inelasticity, the orientation changes sign with scattering deflection angle, indicative of quantum interference effects.
3. We have made the most precise determination of the binding energy of the NO dimer.

Number of Graduate Students:

(3) Vilen Nestorov (partial support), James Barr, Adam Gianola (partial support)

Number of Undergraduates:

(1) George Barnes

Number of postdoctoral Fellows:

(1) Wenwu Chen (partial support)

Publications to date:

"Ion imaging measurement of collision-induced rotational alignment in Ar-NO scattering", J.I. Cline, K.T. Lorenz, E.A. Wade, J.W. Barr, and D.W. Chandler, *J. Chem. Phys.* **115**, 6277-6280 (2001)

"Direct measurement of the preferred sense of NO rotation after collision with argon", K.T. Lorenz, D.W. Chandler, J.W. Barr, W. Chen, G.L. Barnes, and J.I. Cline, *Science* **293**, 2063-2066 (2001)

"Direct measurement of the binding energy of the NO dimer", E.A. Wade, J.I. Cline, K.T. Lorenz, C. Hayden, and D.W. Chandler, *J. Chem. Phys.*, **116**, 4755-4757 (2002)

"Ion imaging applied to the study of chemical dynamics", D.W. Chandler and J.I. Cline, in *Modern Trends in Chemical Reaction Dynamics – Part I*, ed. K.P. Liu and X.M. Yang (World Scientific Pub.), in press 2003.